

HIGH T_g POLYIMIDES FOR RESIN TRANSFER MOLDING

Kathy C. Chuang NASA Glenn Research Center, Cleveland, OH 44135
Jim M. Criss, Jr. M & P Technologies, Inc. Marietta, GA 30068
Eric A. Mintz & Brian Shonkwiler Clark Atlanta University, Atlanta, GA 30314
Daniel A. Scheiman QSS Inc, Cleveland, OH 44135
Baochau N. Nguyen & Linda S. McCorkle Ohio Aerospace Institute, Cleveland, OH 44142
DeNise Hardy-Green University of Akron, Akron, OH 44325

ABSTRACT

A series of new polyimide resins with low-melt viscosities and high glass transition temperatures (T_g's) of 340-350 °C were developed for resin transfer molding (RTM) applications. The viscosities of these polyimide resins, based on 2,3,3',4'-Biphenyltetracarboxylic Dianhydride (a-BPDA), are in the range of 10-30 poise. The composites were fabricated successfully at 260-280 °C with a pot life of 30-60 minutes by the RTM process. The viscosity profiles of the polyimide resins and the mechanical properties of the polyimide carbon fiber composites will be discussed.

KEY WORDS: Polyimide, Phenylethynyl Endcap, Resin Transfer Molding (RTM), High Temperature Composites, 2,3,3',4'-Biphenyltetracarboxylic Dianhydride (a-BPDA)

1. INTRODUCTION

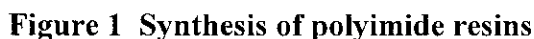
Polyimide/carbon fiber composites have been used successfully as lightweight materials in place of alloys of aluminum, steel and titanium in aerospace components used for high temperature applications for the past 25 years. While the thermoplastic polyimide Avimid N[®] [1], based on 6F-dianhydride and a 95/5 mixture of *p*-phenylenediamine (*p*-PDA) and *m*-phenylenediamine (*m*-PDA), is probably one of the most thermally stable polyimides; however, the processing of high molecular weight polyamic acid requires the use of a high boiling solvent, N-methyl-2-pyrrolidinone (NMP), which is very difficult to remove and often generates voids during composite fabrication. PMR-15 [2] was developed using the polymerization of monomer reactants approach with benzophenone-tetracarboxylic diester diacid (BTDE), 4,4'-methylene dianiline (4,4'-MDA) and the nadic ester (NE) endcap in low boiling methanol. The use of oligomers with the reactive nadic endcap improved the processability and enabled the fabrication of large PMR-15 composite parts as replacements for heavier metallic components in aircraft engines.

* This paper is declared a work of the U.S. government and is not subjected to copy right protection in the United States.

However, the diamine (4,4'-MDA) used in the PMR-15 formulation is toxic and poses a health threat when used in the monomer form in prepregs. Ideally, the aerospace industry would benefit from low-cost manufacturing of composites using a resin transfer molding (RTM) process. Attempts have been made to fabricate PMR-type polyimides by solvent assisted resin transfer molding (SaRTM) or infusion techniques [3] with some success, including the fabrication of a GE-90 center vent tube [4]. The drawback of SaRTM processed polyimide composites is the higher void content ($\geq 5\%$) than what is acceptable for aerospace primary structures ($<2\%$).

Recently, substantial efforts have been devoted to the development of solvent-free imidized powders as RTM resins that would exceed the $232\text{ }^{\circ}\text{C}$ ($450\text{ }^{\circ}\text{F}$) performance capability of state-of-the-art bismaleimides, such as BMI-5270-1. One approach adopted by the Maverick Corporation used the diester diacid of benzophenonetetracarboxylic dianhydride (BTDE) along with the nadic ester endcap, similar to the making of the PMR-15 imidized powder, but substituted 4,4'-methylene dianiline (MDA) with a combination of a flexible 4,4'-[1,3-phenylene-bis(1-methylethylidene)] (i.e. Bisaniline M) and rigid *m*-phenylenediamine (*m*-PDA) at a lower molecular weight formulation. These RTM processable PMR-type polyimides exhibited low-melt viscosities of 3-10 poise as recorded by a Brookfield viscometer at $260\text{ }^{\circ}\text{C}$. They also displayed glass transition temperatures (T_g 's) in the range of $260\text{--}300\text{ }^{\circ}\text{C}$, making them suitable for $260\text{ }^{\circ}\text{C}$ ($500\text{ }^{\circ}\text{F}$) applications [5]. In pursuit of higher temperature capability and wider processing window, NASA Langley developed a series of phenylethynyl terminated imide (PETI) oligomers with low-melt viscosities (complex $[\eta]^* \sim 10$ poise as measured by rheometer at $280\text{ }^{\circ}\text{C}$) for resin transfer molding. PETI-298 was prepared from symmetrical 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) formulated with 1,3-bis(3-aminophenoxy)benzene (1,3,3-APB), 3,4'-oxydianiline(3,4'-ODA) and endcapped with 4-phenylethynylphthalic anhydride (PEPA) to afford a resin with $T_g = 298\text{ }^{\circ}\text{C}$ [6]. Recent studies have shown that polyimides derived from asymmetrical 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) often exhibit lower viscosities and higher T_g s than that of 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) based polyimides [7]. For example, PETI-330 ($T_g = 330\text{ }^{\circ}\text{C}$) formulated with asymmetrical 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) and PEPA endcap along with a mixture of 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB) and *m*-phenylenediamine (*m*-PDA) displayed a better property retention at $288\text{ }^{\circ}\text{C}$ than PETI-298, due to its higher T_g and softening temperature [8]. To advance the high temperature capability up to $315\text{ }^{\circ}\text{C}$ ($600\text{ }^{\circ}\text{F}$), PETI-375 [9] was developed using the same monomers as PETI-330 except that 2,2'-bis(trifluoromethyl)benzidine (BTBZ) was used in place of *m*-phenylenediamine. The use of BTBZ raised the resin T_g to $375\text{ }^{\circ}\text{C}$, but it also increased resin cost substantially, because BTBZ is expensive. PETI-298, PETI-330 and PETI-375 all can be processed by resin transfer molding (RTM) to yield composites with low void content and excellent mechanical properties for applications between $260\text{--}315\text{ }^{\circ}\text{C}$. However, the process to synthesize these imidized oligomers required refluxing the monomers in *N*-methyl-2-pyrrolidinone (NMP) at $\sim 185\text{ }^{\circ}\text{C}$ and removing water formed in the reaction mixture by azeotropic distillation using toluene. To afford the imidized powder, the oligomer solution was poured into water and the resultant solid was isolated and dried in a forced air oven at $135\text{ }^{\circ}\text{C}$ for 24 hours until it reached a constant weight to

In an effort to develop a simpler and more cost effective way to produce solvent-free polyimides for resin transfer molding, a-BPDA and 4-phenylethynylphthalic anhydride (PEPA) were mixed with either 3,4'-oxydianiline (3,4'-ODA) or 3,4'-methylenedianiline (3,4'-MDA). Then the powdery monomer mixture was heated until all three monomers were melted and then the resultant oligomers endcapped with the reactive phenylethynyl group were ground into powders. This approach uses no solvent in the process and the only volatile generated is water formed during the imidization process.



2.1 Resin Preparation and Characterization

2.2 Composite Fabrication

Composite panels were fabricated using a high temperature RTM process [10, 11]. The panels were made from T650-35, 8 harness satin weave (8HS) carbon fabrics with an 8 ply quasi-isotropic lay-up [+45/0/90/-45]_s. After the tool and the injector were preheated to approximately 288 °C, 600 gm of the resin was injected at 1.38 MPa and then cured at 371 °C for 2 hours, followed by a postcure in an oven at 343 °C (650 °F) for 8 hours to achieve the optimal mechanical properties at elevated temperature.

3. RESULTS AND DISCUSSION

3.1 Physical properties and viscosity profiles of neat resins

The resin based on a-BPDA with phenylethynyl endcap and formulated with 3,4'-oxydianiline (3,4'-ODA) exhibited a T_g of 370 °C by TMA after postcure, and is designated as RTM370. The resin derived from 3,4'-methylenedianiline (3,4'-MDA) had a T_g of 350 °C, and is designated as RTM350.

Table 1 Physical Properties of Imide Oligomers Based on a-BPDA and PEPA

Resin	Diamine	Min. η @280 °C by Brookfield ¹ (Poise)	Min. Complex [η] [*] @280°C ² (Poise)	T_g (°C) NPC ³ by TMA	T_g (°C) PC ⁴ @ 650°F By TMA ⁵
RTM370	3,4' -ODA	14	11	342	370
RTM350	3,4' -MDA	7.4	20	338	350

¹ Absolute viscosity measured by Brookfield Viscometer at 280 °C.

² Complex viscosity measured by Aries Rheometer, using parallel plates.

³ NPC = No Postcure

⁴ PC = Postcured at 343 °C (650 °F) for 16 hrs.

⁵ TMA = Thermal mechanical analysis heated at 10 °C/min. using expansion mode.

Table 1 shows that the absolute viscosity of RTM370, as measured by the Brookfield Viscometer, remained steady below 20 poise for 1 hour, whereas the viscosity of RTM350 dropped well below 10 poise initially, but climbed up to 20-30 poise within 30-60 minutes (Fig. 2). In practice, a resin viscosity between 10-30 poises with 1 hour pot-life (reasonable viscosity within processing window) is feasible for the resin transfer molding (RTM) process. The rheology profile of RTM370 showed a minimum complex viscosity, [η]^{*} = 11 poise, and maintained a viscosity below 30 poise for 20-30 min. (Fig.3) In contrast, RTM350 displayed a minimum complex viscosity, [η]^{*} = 20 poise, and had a shorter pot-life than RTM370 (Fig.4). The complex viscosities, [η]^{*}, measured by the rheometer are different from the Brookfield viscometer measurement, because they are dependent on the experimental settings in terms of torque and tension and can vary significantly. Nevertheless, the absolute viscosities recorded by the Brookfield viscometer are more consistent and reproducible. The shorter pot-life of RTM350 arises from the presence of methylene group (-CH₂-) in 3, 4'-methylenedianiline as compared to the oxygen linkage (-O-) in 3,4'-oxydianiline within RTM370. The methylene unit is believed to produce a stable benzylic free radical during the cure, which can promote further crosslinking; thus, contributing to the increase in viscosity in various imide oligomers containing -CH₂- units. However, the additional crosslinking promoted by the methylene group, though not yet verified, generally yields better thermo-oxidative stability than the ether linkage [12,13]. This trend is further confirmed by the superior thermo-oxidative stability of PMR-15 composites which contains 4,4'-methylenedianiline, relative to RP-46 based on 3,4'-oxydianiline [14].

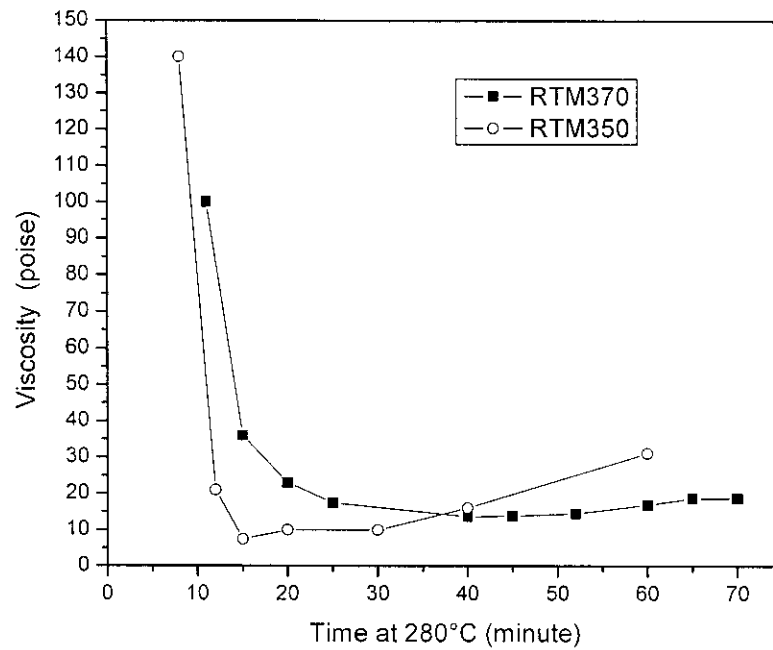


Fig. 2 Absolute Viscosity by Brookfield Viscometer at 280 °C

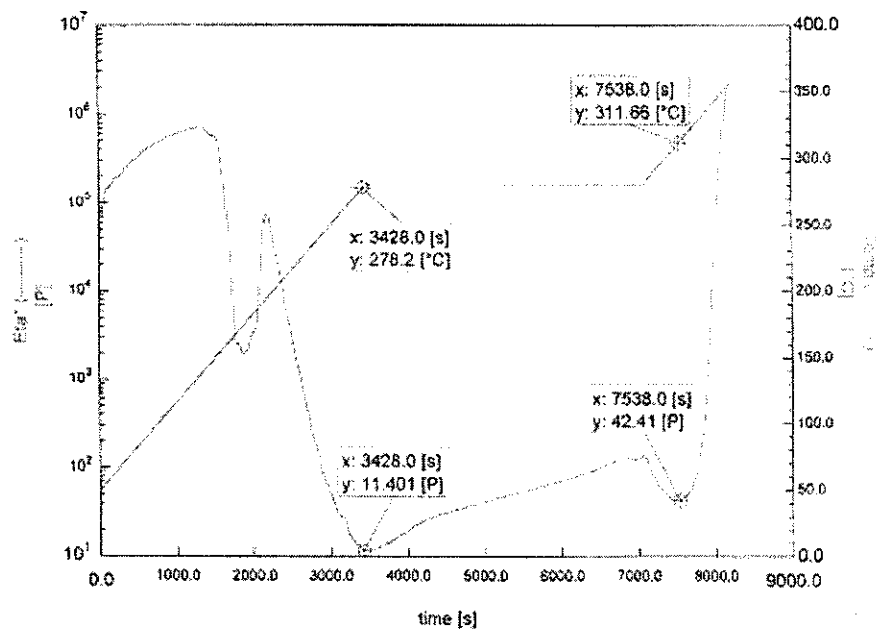


Fig. 3 Rheology of RTM 370

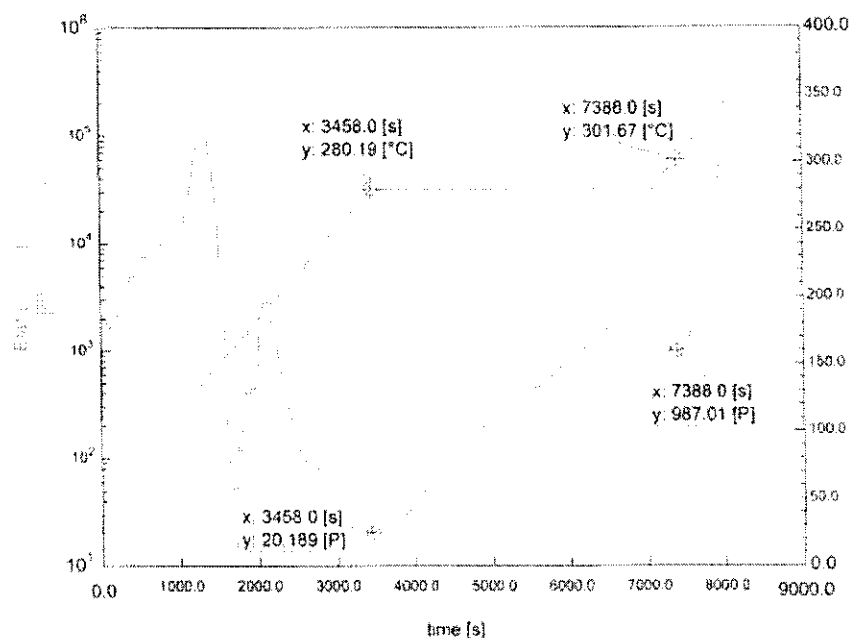


Fig. 4 Rheology of RTM350

3.2 Characterization and mechanical properties of polyimide/T650-35 composites

The T650-35 carbon fabric reinforced composites of RTM370 and RTM350 polyimides displayed a T_g of 356 °C and 337 °C, respectively, after postcure at 343 °C (650 °F). (Table 2). The T_g 's of these phenylethynyl terminated polyimide composites were generally 15-20 °C lower than that of the corresponding neat resins. RTM370 resin has good flow due to its low viscosity, and the corresponding composite exhibits very uniform resin distribution and no voids as shown in Scanning Electron Micrograph (Fig. 5a). Due to resin's higher viscosity and shorter pot-life, the overall quality of RTM 350 composite is not very consistent throughout the panel; however, the void content was still low (~1% by acid digestion) in majority of the panel as shown in Fig.5b. Additional effort is needed to yield more uniform composites with RTM350.

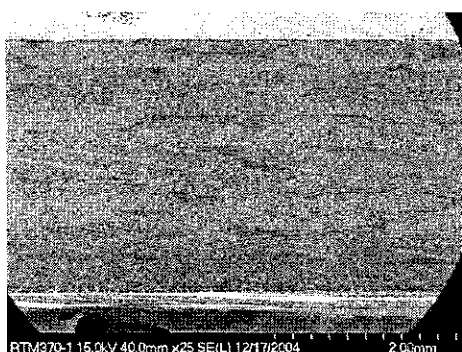
Table 2 T_g s of Polyimide/T650-35 Composites based on a-BPDA and PEPA

Resin	Diamine	T_g (°C) by DMA ¹ NPC ²	T_g (°C) by DMA PC ³ @ 650°F
RTM370	3,4'-ODA	324	356
RTM350	3,4'-MDA	314	337

¹ DMA= Dynamic Mechanical Analysis were performed at 5 °C/min heating rate, using single cantilever.

² NPC = No postcure.

³ PC = Postcured at 343 °C (650 °F) for 8 hours.



a) RTM 370



b) RTM350

Figure 5 Scanning electron micrographs of RTM370 and RTM 350 composites

Postcure of polyimide composites was conducted to achieve optimal mechanical properties at elevated temperature. As shown in Table 3, both RTM370 and RTM350 composites exhibited outstanding open-hole compression strength (Fig. 6) and modulus (Fig. 7) at 288 °C (550 °F), relative to BMI-5270-1 ($T_g = \sim 300$ °C) whose expected performance temperature was only around 232 °C (450 °F). RTM370 also retained $\sim 75\%$ of its room temperature compression strength at 288 °C, and $\sim 55\%$ of its initial strength at 315 °C (600 °F). The open-hole compression modulus retention for RTM370 was 95% at 288 °C and 85% at 315 °C, respectively. However, both the open-hole compression strength and modulus of RTM370 at 327 °C (620 °F) were much higher than that of 315 °C. This unusual, but desirable phenomenon is probably derived from the additional crosslinking of phenylethynyl groups at the higher test temperature of 327 °C. Furthermore, RTM350 exhibited higher OHC strength than RTM 370 at 315 °C, which is likely due to the presence of stable methylene linkages, even though RTM350 displayed a lower T_g than RTM370. At 288 °C (550 °F), RTM 370 and RTM350 maintained 70% and 65% of their short beam shear strength at room temperature, respectively (Fig. 8).

Table 3. Mechanical Properties of RTM370 and RTM 350 versus BMI-5270-1

Properties	Test Tem. (°C)	RTM 370	RTM 350	BMI-5270-1
OHC Strength (MPa)	23	306	285	245
	288	223	216	148
	315	166	199	---
	327	211	---	---
OHC Modulus (GPa)	23	50	43	51
	288	47	44	38
	315	42	45	---
	327	56	---	---
SBS Strength (MPa)	23	62	58	37
	288	43	38	14

OHC = Open-Hole Compression

SBS = Short Beam Shear

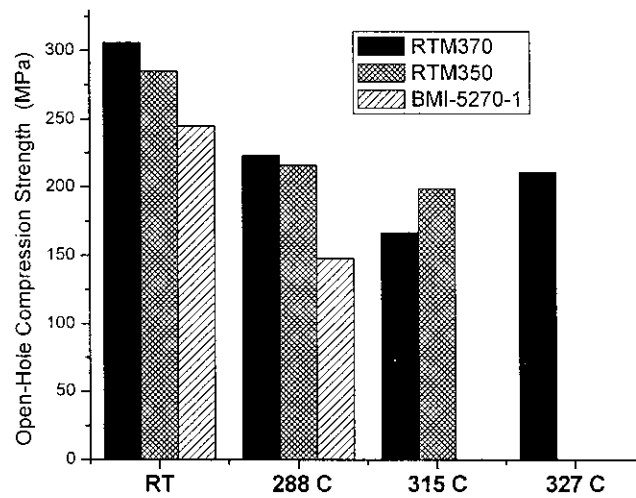


Fig. 6 Open-Hole Compression Strength of RTM370 and RTM350

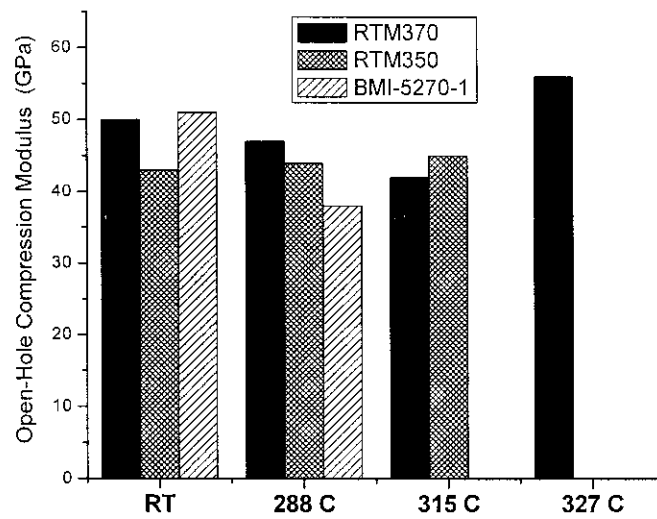


Fig. 7 Open-Hole Compression Modulus of RTM370 and RTM350

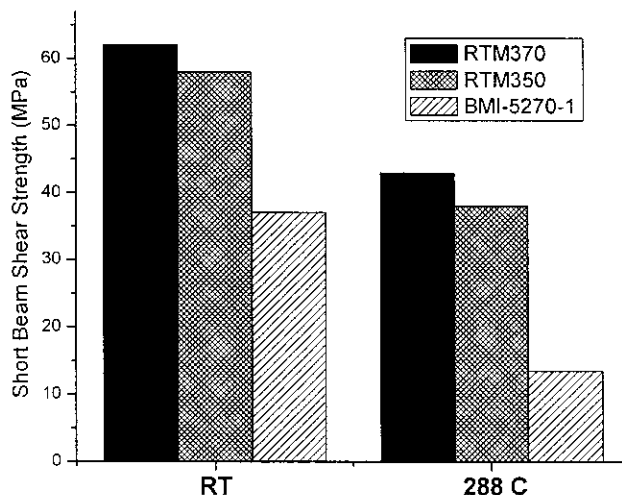


Fig. 8 Short Beam Shear Strength of RTM370 and RTM350

4. CONCLUSION

A new series of imide oligomers based on asymmetrical 2,3,3',4'-benzophenone-tetracarboxylic dianhydride (a-BPDA), and terminated with the 4-phenylethynylphthalic anhydride (PEPA) endcap, were formulated with 3,4'-oxydianiline (designated RTM370) and 3,4'-methylenedianiline (RTM350) in a melt without any solvent. Both RTM370 and RTM350 displayed low-melt viscosities in the range of 10-30 poise with 1 hour of pot-life as measured by the Brookfield viscometer. These low-melt resins were successfully injected to T650-35 carbon fabrics by the resin transfer molding (RTM) process at 280 °C to produce composites with low voids. The absence of organic solvents involved in the preparation of imide oligomers offered easy processing by RTM, which should result in savings in manufacturing cost. Both RTM370 and RTM350 exhibited excellent open-hole compressive strength and modulus, and retained 75% of their room temperature properties at 288 °C. Accordingly, RTM370 and RTM350 also maintained 70% and 65% of their initial shot beam shear strength at 288 °C, respectively. Most importantly, due to their high T_g s, both RTM370 and RTM350 exhibited outstanding property retention for potential application at 315 °C (600 °F).

5. REFERENCES

- 1) H.H. Gibbs, J. Appl. Polym. Sci., **35**, 297 (1979).
- 2) T.T. Serafini, P. Delvigs, G.R. Lightsey, J. Polym. Sci., Chem. Ed., **16**, 905 (1972).
- 3) K.C. Chuang, D.S. Papadopoulos, C.P. Arendt, Int'l SAMPE Sym., **42(2)**, 283 (1997).
- 4) R.D. Vannucci, R. Gray, D.A. Scheiman, Proceedings of HITEMP Review 1999, NASA / CP-1999-208915, Vol.1, paper no. 4, pp1-9
- 5) R.A. Gray and L.R. McGrath, SAMPE J., **40 (6)**, 23 (2004).
- 6) J.G. Smith, Jr., J.W. Connell, P.M. Hergenrother, R. Yokota, J.M. Criss, Int'l SAMPE Sym., **47, Vol. 1**, 316 (2002)
- 7) M. Hasegawa, Z. Shi, R. Yokota, F. He, H. Ozawa, High Perf. Polym., **13**, 355 (2001)
- 8) J.W. Connell, J.G. Smith, Jr., P.M. Hergenrother, High Perf. Polym., **15**, 375 (2003).
- 9) J.W. Connell, J.G. Smith, Jr., P.M. Hergenrother, J.M. Criss: High Temperature Transfer Molding Resins: Preliminary Composite Properties of PETI-375, Proceedings of 48th Int'l SAMPE Sym., CD Version (2003).
- 10) J.G. Smith Jr., J.W. Connell, P.M. Hergenrother, J.M. Criss, Int'l SAMPE Sym., **45**, 1584 (2000).
- 11) J.M. Criss, R.W. Koon, P.M. Hergenrother, J.W. Connell, J.G. Smith, Jr., SAMPE Tech. Conf., **33**, 1009 (2001).
- 12) W.B. Alston, Polym. Prep., **27(2)**, 4410 (1986).
- 13) W.B. Alston, Polym. Prep., **33(1)**, 428 (1992)
- 14) W.E. McCormack, Results of GEAE's Low-cost, Non-MDA PMR-15 Replacement Program, High Temple Workshop XVI, N-1 (1996).